

Laboratory Manager Approval: Ralph Schulz / 08/24/2021
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**LABORATORY SOP FOR EPA METHOD 5035:
VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS
SPECTROMETRY (GC/MS):CAPILLARY COLUMN TECHNIQUE**

Access to this SOP shall be available within the laboratory for reference purposes; the official copy of this SOP resides on the official Georgia EPD website at <https://epd.georgia.gov/about-us/epd-laboratory-operations>. Printed copies of this SOP will contain a watermark indicating the copy is an uncontrolled copy.

PURPOSE: This SOP is promulgated to insure consistent operation of the GC/MS system within the GC/MS laboratory for EPA Method 8260B. It is intended as a guide for the daily operation of the instrument as well as a reference for maintenance, troubleshooting, and quality control.

Note: All footnote references are to Method 8260B sections, unless otherwise noted.

1.0 Scope and Application

- 1.1 This method is to minimize the loss of volatile organic compounds during the sampling in the field and in the sample preparation within the laboratory. This method is designed for low levels of volatile organic compounds in solid materials (e.g. soils, sediments, and solid wastes). This method is also provided for sampling and preparing solid samples containing high VOC concentrations and oily wastes. The following compounds are currently analyzed using this method:

<u>Compound</u>	<u>CAS No.</u>
Acetone	67-74-1
Acrylonitrile	107-13-1
Benzene	71-43-2
Bromobenzene	108-86-1
Bromochloromethane	74-97-5
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane	74-83-9
2-Butanone	78-93-3
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7

Chloroethane	75-00-3
Chloroform	67-66-3
Chloromethane	74-87-3
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
Cyclohexane	00110-82-7
1,2-Dibromo-3-chloropropane	96-12-8
Dibromochloromethane	124-48-1
1,2-Dibromomethane	106-93-4
Dibromomethane	74-95-3
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
trans-1,4-Dichloro-2-butene	110-57-6
Dichlorodifluoromethane	75-71-8
1,1-Dichloroethane	75-34-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-4
cis-1,2-Dichloroethene	156-59-2
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5
1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	594-20-7
1,1-Dichloropropene	563-58-6
cis-1,3-Dichloropropene	10061-01-5
trans-1,3-Dichloropropene	10061-02-6
Ethylbenzene	100-41-4
Hexachlorobutadiene	87-68-3
2-Hexanone	591-78-6
Iodomethane	74-88-4
Isopropylbenzene	98-82-8
p-Isopropyltoluene	99-87-6
Methyl acetate	0079-20-9
Methylene chloride	75-09-2
Methyl tert-butyl ether	1634-04-4
4-Methyl-2-pentanone	108-10-1
Naphthalene	91-20-3
Methylcyclohexane	00108-87-2
n-Propylbenzene	103-65-1
Styrene	100-42-5
1,1,1,2-Tetrachloroethane	630-20-6
1,2,3-Trichloropropane	96-18-4
1,1,2-Trichlorotrifluoroethane	00076-13-1
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8
1,1,2,2-Tetrachloroethene	79-34-5
Tetrachloroethene	127-18-4
Toluene	108-88-3

1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trichlorobenzene	120-82-1
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene	79-01-6
Trichlorofluoromethane	75-69-4
Vinyl acetate	75-01-4
Vinyl chloride	75-01-4
m-Xylene	108-38-3
o-Xylene	95-47-6
p-Xylene	106-42-3.

Surrogate Standards

Bromofluorobenzene(Surr.)	460-00-4
Dibromofluoromethane(Surr.)	1868-53-7
1,2-Dichloroethane-d4(Surr.)	17060-07-0
Toluene-d8(Surr.)	2037-26-5

Internal Standards

Chlorobenzene-d5(I.S.)	3114-55-4
1,4-Dichlorobenzene-d4(I.S.)	3855-82-1
1,4-Difluorobenzene(I.S.)	540-36-3
Pentafluorobenzene(I.S.)	363-72-4

- 1.2 Low concentration soil method-generally applicable to soils and other solid samples with analyte concentrations <400 ug/Kg. The sample can be collected using an EnCore sampler and preserved in a preweighed vial that already contains a stirring bar and sodium bisulfate solution. The sample must be preserved within 48-hour period after sampling. Preserving the sample extends the holding time to 14 days. The vial is capped and placed into the Closed-system purge-and-trap system. Immediately before analysis, 5mL organic free reagent water, internal and surrogate mix standard are automatically added without opening the vial. The sample vial is then heated to 40⁰C and purged for 11 minutes with the bar stirring on. Purged analytes travel via a transfer line to a trap. When purging is complete the trap is heated to 245⁰C for desorb preheat mode, heated to 250⁰C in the desorb mode, then back flush with Helium to desorb the sample into a gas chromatograph instrument for analyzing.
- 1.3 High concentration soil method-applicable to soils with concentrations greater than 400 ug/Kg. The sample is weighed out into 20mL vial from an Encore soil coring body and 5 mL purge and trap grade Methanol added. Methanol acts as an extraction fluid and the Methanol extraction becomes the actual representation of the sample being used. The holding time is 14 days from the extraction. Before processing sample for analysis, withdraw 100 uL or less depending on how high concentrations from the sample's screening of this extract (Refer to Headspace-7 Rev.2 SOP), and spike into a preweighed vial that contained a stirring bar and sodium bisulfate solution. Place the vial into the Closed-system purge-and-trap system. Immediately before analysis, 5mL of sample, 1uL of surrogate-internal standard mixture are automatically withdrawn, added and transferred in a purge without opening the vial. The

sample vial is then heated to 40°C and purged for 11 minutes with the bar stirring. on. Purged analytes travel via a transfer line to a trap. When purging is complete the trap is heated to 245°C for desorb preheat mode, heated to 250°C in the desorb mode, then back flush with Helium to desorb the sample into a gas chromatograph instrument for analyzing

- 1.4 High concentrations oily waste method-applicable to oily samples with volatile concentrations greater than 400 ug/Kg that can be diluted in a water miscible solvent.

2.0 Definitions

Refer to Chapter 3 of the Georgia EPD Laboratory Quality Assurance Manual for Quality Control definitions.

3.0 Interferences

- 3.1 Daily analysis of sodium bisulfate blanks is used to determine if there are any background interferences before actual samples are run. There is a potential for organic compounds to be present on unclean glassware, syringes, purge-and-trap lines, and GC system lines. If unacceptable levels of contamination are found following the blank run, the problem must be corrected and another blank run to show that the system is free of contamination.

SUBTRACTING BLANK VALUES FROM SAMPLE RESULTS IS NOT PERMITTED.

A sodium bisulfate blank should be run after samples with high concentrations of compounds to prevent any carryover into the next sample being run. Check this blank for acceptable levels of background interference. Run as many blanks as necessary to cleanup contamination.

- 3.2 Special precautions must be taken to reduce Methylene chloride contamination of the volatiles laboratory. Methylene chloride is the solvent used in the semi-volatiles and extractions laboratories, as well as being an 8260 analyte; therefore it is extremely important to not share glassware or apparatus between these laboratories. Methylene chloride is persistent and is very hard to get rid of after a contamination occurs.
- 3.3 A trip blank of sodium bisulfate is taken through the sampling process to indicate any interferences created by the sampling procedure.

4.0 Safety

Refer to Laboratory Chemical Hygiene Plan.

5.0 Apparatus and Equipment

- 5.1 Sample Container: 40mL preweighed glass vial that already contains a stirring bar, sodium bisulfate solution and screw-cap with a PTFE faced silicon septum.
- 5.2 Purge and Trap System: The Archon Purge and Trap autosampler system automatically adds the surrogate and internal standards, reagent water to the sample vial, then heats the vial to 40°C while agitating the contents while the

inert purge gases pass through the sample. The Archon collects the headspace vapors and transfer the vapors to the absorber trap.

- 5.3 The Tekmar 3000and/or Velocity purge-and-trap controls the introduction of the sample from the Archon purge vessel onto the trap. If the trap is newly installed, the trap MUST be preconditioned according to manufacture's specifications found on the enclosed data sheet. Once the sample is purged onto the trap and the GC is ready, the purge-and-trap will then heat the trap and introduce it to the GC.
- 5.4 Library NBS75K or Wiley 275 are used for spectra comparison searches
- 5.5 Syringes-gas tight glass syringes from 10 uL to 1 mL.
- 5.6 Top loading balance-Capable of accurately weighing to 0.01 grams. (Mettler AT200,Mettler PB4002)
- 5.7 Volumetric Flask- Class A, 10 mL, 50 mL and 100 mL.
- 5.8 Spatula, stainless steel-narrow enough to fit into a sample vial.
- 5.9 Disposable Pasteur pipettes.
- 5.10 Magnetic stirring bars- PFTE or glass coated.
- 5.11 Encore sampler or the equivalent.

6.0 Reagents

- 6.1 Organic free reagent water-All references to water in this method refer to organic free reagent water.
- 6.2 Organic residue grade methanol for cleanup of glassware and autosampler valves.
- 6.3 Purge-and-trap grade methanol for standards and waste level sample preparations.
- 6.4 Certified Stock standard solutions prepared according to 8260B procedure.
- 6.5 Internal and surrogate standard mixes prepared as a secondary dilution at a concentration of 250 ug/mL. This solution is placed in a standard vial in the Archon. An injection of 1.0 uL of this standard into a 5 mL samples yields a IS+SS concentration of 50 ug/l.

Surrogate Standards

Bromofluorobenzene(Surr.)
Dibromofluoromethane(Surr.)
1,2-Dichloroethane-d4(Surr.)
Toluene-d8(Surr.)

Internal Standards

Chlorobenzene-d5(I.S.)
1,4-Dichlorobenzene-d4(I.S.)
1,4-Difluorobenzene(I.S.)
Pentafluorobenzene(I.S.)

- 6.6 Certified Bromofluorobenzene stock solution prepared according to 8260B procedure.
- 6.7 Calibration standards are prepared in pre-made NaHSO₄ solution vials from the stock standard solution. A seven-point curve is prepared at the concentrations of 2, 5, 50 , 100, 150, 200, and 400 ug/Kg.

- 6.8 Certified matrix spike standard consisting of 1,1-dichloroethene, Trichloroethene, Chlorobenzene, Toluene, and Benzene. Its final concentration in the vial is 250 ug/mL. It is placed in a standard vial in the Archon. 1.0 uL of this matrix spike is injected into each 5 mL of spike or duplicate sample, yielding a final sample concentration of spike components of 50 ug/Kg.
- 6.9 Sand can be purchased prepared and certified from chemical suppliers.
- 6.10 Precertified Sodium bisulfate solution.

7.0 Sample Collection

Refer to Chapter 5 of the Georgia EPD Laboratory Quality Assurance Manual for Sample Container, Sample Preservation and Sample Holding Times.

8.0 Calibration

Refer to the 8260B procedure for calibration information.

9.0 Quality Control

- 9.1 Three aliquots of the same sampling site should be taken and prepared together. During the analysis, two of the samples should be spiked and used as a matrix spike and a matrix spike duplicate.
- 9.2 Two blank vials containing approximately 5g of prepared and certified sand in 5mL of sodium bisulfate solution prepared at the start of sample extraction must be analyzed with the samples. One vial is the prep open and the cap should remain off during the entire extraction process and may be recapped when extraction is complete. The other vial is the prep closed and the cap should remain on the vial throughout the extraction process.
- 9.3 An LCS and an LCS Duplicate must be prepared and analyzed with the samples.

10.0 Procedure

Samples must be preserved within 48 hours of sampling and analyzed within 14 days of the sampling date.

10.1 Low concentration soil samples

- 10.1.1 Label sample ID on each 40 mL vial which contains 5mL prepared and certified Sodium bisulfate solution.
- 10.1.2 Place vial on balance and tare balance.
- 10.1.3 Remove Encore sampler from pouch. Twist locking stem to release plunger. Break side clips from cap and remove cap. Quickly invert encore over vial and depress plunger to remove sample plug. Cap vial and return to balance.
- 10.1.4 Label sample weight on vial.
- 10.1.5 Record weight to the nearest 0.01 g, date preserved, lot number and type of preservative and analyst name in the sample preservation logbook.
- 10.1.6 Shake vial until mixed before analysis. If samples are not to be run immediately, store sample at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$. The storage area should be free from organic solvent.

10.2 High concentration soil samples

- 10.2.1 Record sample ID on each 20mL vial.
- 10.2.2 Place each 20 mL vial on balance and tare balance.

- 10.2.3 Remove Encore sampler from pouch. Twist locking stem to release plunger. Break side clips from cap and remove cap. Quickly invert encore over vial and depress plunger to remove sample plug. Cap vial and return to balance.
- 10.2.4 Label sample weight, analyst, date, volume and lot number of preservation on vial.
- 10.2.5 Add 5mL of methanol (purge and trap grade) to vial. Cap vial.
- 10.2.6 Record weight to the nearest 0.01 g, date preserved, lot number and type of preservative and analyst name in the sample preservation logbook.
- 10.2.7 Place vial on vortex and agitate until mixed if necessary.
- 10.2.8 Sample extraction may now be diluted into a vial that contains a stirring bar and preweighed sodium bisulfate solution (50X is the lowest dilution that meets report limit requirement). Samples analyzed according to Method 8260B SOP for soil procedure. If samples are not to be run immediately, store samples at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$. The storage area should be free from organic solvent.

11.0 Calculations

N/A (See Method 8260B for analysis calculations.)

12.0 References

- 12.1 Method 5035 Closed-System Purge and Trap and Extraction for Volatile Organics in Soil and Waste Samples. SW846B

13.0 Reporting Limits(RLs), Precision and Accuracy Criteria, and Quality Control Approach.

N/A (See Method 8260b or associated SOP for method data).

PRESAMPLING

1. Schedule sampling with the laboratory.
Steve Bryan - GC-Mass Spec Laboratory
Phone - (404)206-5260
2. Pickup EnCore sampler tool, an one 4oz jar (for screening) per sampling site.
3. Pickup four EnCore™ samplers if both high and low level analysis(ppb) is needed, or one EnCore™ sampler if only high level(ppm) analysis is needed per sampling site.

Field sampling

1. Fill the 4oz jar with the sample allowing minimum headspace.
2. Remove the sampler from the package and attach the sampling handle tool.
(low level(ppb) - three EnCore™ samplers per site)
3. Quickly collect a 5-gram sample using the EnCore™ sampler.
4. Attach the EnCore™ sampler cap.
5. Fill out the label with the sample information and attach to the sample.
Immediately cool sealed samplers on ice.
6. Ship to the laboratory the same day.

Laboratory analysis

1. Within 48 hours of sampling, transfer one EnCore™ sampler to a tared vial containing purge and trap grade methanol.
2. Record sample weight.
3. Analyze according to EPA Method 8260 for high level samples.
4. If low level analysis is needed, transfer another EnCore™ to a vial containing Sodium Bisulfate.
5. Analyze according to EPA Method 5035 and 8260 for low level VOCs in soil.

Attachment: Disposable EnCore™ sampler instruction sheet

(Shipping Attachment B)

Disposable
En Core™ Sampler

Sampling Procedures

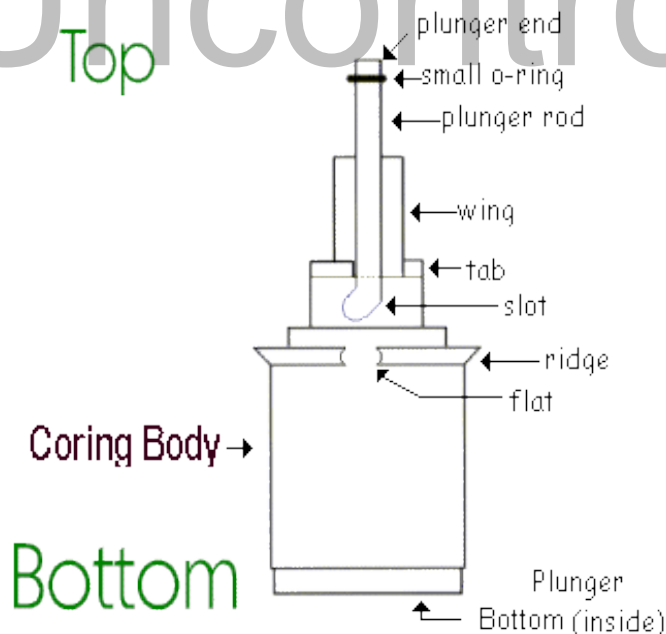
NOTE:

1. EnCore Sampler is a Single Use device. It cannot be cleaned and/or reused.
2. EnCore Sampler is designed to store soil. Do not use En Core Sampler to store solvent or free product!
3. En Core Sampler must be used with En Core™ T-Handle and/or En Core™ Extrusion Tool exclusively. (These items are sold separately.)

Using The En Core™ T-Handle

Before Taking Sample:

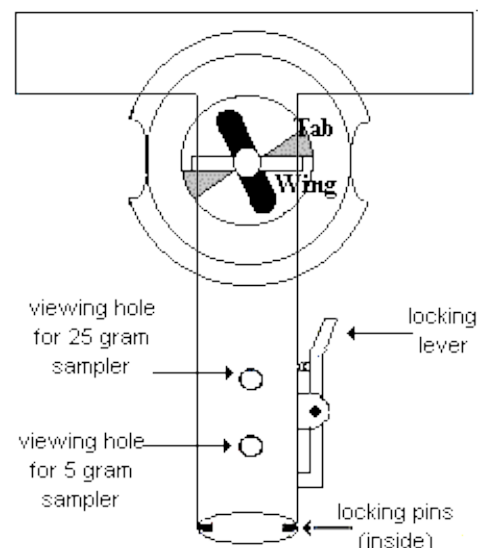
1. Hold coring body and push plunger rod down until small o-ring rests against tabs. This will assure that plunger moves freely.
2. Depress locking lever on En Core T-Handle. Place coring body, plunger end first, into open end of T-Handle, *aligning the (2) slots on the coring body with the (2) locking pins in the T-Handle*. Twist coring body clockwise to lock pins in slots. Check to ensure sampler is locked in place. Sampler is ready for use.



Taking Sample:

3. Turn T-Handle with T-up and coring body down. This positions plunger bottom flush with bottom of coring body (ensure that plunger bottom is in position). Using T-Handle, push Sampler into soil until coring body is completely full. When full, small o-ring will be centered in T-Handle viewing hole. Remove Sampler from soil. Wipe excess soil from coring body exterior.

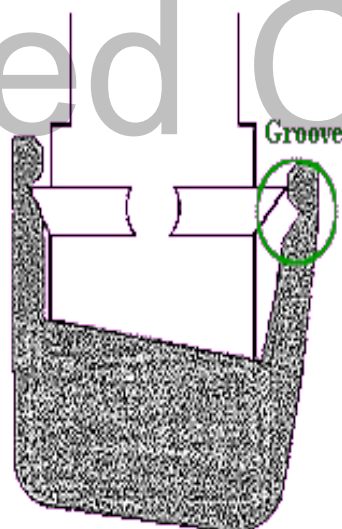
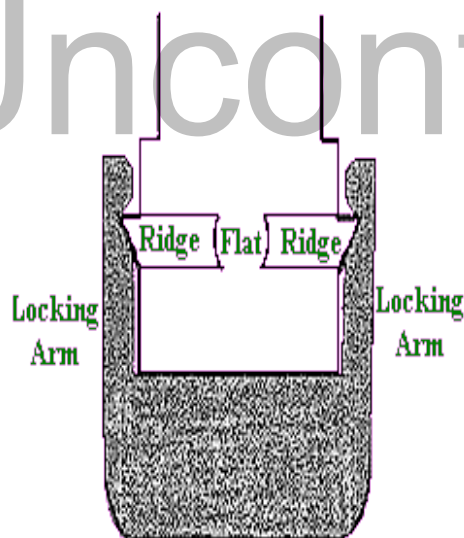
4. Cap coring body while it is still on T-handle. Push cap over flat area of ridge. Push and twist cap to lock arm in place. Cap must be seated to seal sampler (see diagram below).

**Sampler Correctly Capped**

Locking arm grooves seated over coring body ridge.

Sampler Incorrectly Capped

Cap appears crooked; locking arm grooves not fully seated over coring body ridge

**Preparing****Sampler For Shipment:**

5. Remove the capped Sampler by depressing locking lever on T-Handle while twisting and pulling Sampler from T-Handle.

6. Lock plunger by rotating extended plunger rod fully counter-clockwise until wings rest firmly against tabs (see plunger diagram at right).

7. Attach completed label (from En Core Sampler bag) to cap on coring body.

8. Return full En Core Sampler to zipper bag. Seal bag and put on ice.